2002-338228

[Claims]

[Claim 1] A meso-structure thin film formed by applying a precursor solution containing a surfactant and an inorganic oxide precursor material on a substrate using a centrifugal force, wherein tube like pores in the thin film are oriented almost parallel to the direction of the centrifugal force applied to the substrate.

[Claim 2] The meso-structure thin film according to claim 1, wherein the tube like pores are filled with the surfactant.

[Claim 3] The meso-structure thin film according to claim 1, wherein the meso-structure thin film comprises a hollow structure formed by removing the surfactant from the tube like pores.

[Claim 4] A method for forming the meso-structure thin film by applying a precursor solution containing a surfactant and an inorganic oxide precursor material on the substrate by spin coating, comprising: the steps of preparing the precursor solution containing the surfactant and the inorganic oxide precursor material; holding the substrate outside the rotation center of a spin coater; and placing the precursor solution on the substrate and applying the solution by spin coating to form the meso-structure thin film.

[Claim 5] A method for forming the meso-structure thin film by applying a precursor solution containing a surfactant and an inorganic oxide precursor material on the substrate by spin coating, comprising: the steps of preparing the precursor

solution containing the surfactant and the inorganic oxide precursor material; or holding the substrate outside the rotation center of a spin coater; placing the precursor solution on the substrate and applying the solution by spin coating to form the meso-structure thin film; and removing the surfactant from tube like fine pores in the formed meso-structure thin film to form a hollow structure.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] The present invention relates to the application of an inorganic oxide porous material to be used for catalysts and adsorbents, and more particularly to a meso-structure thin film and manufacturing method therefor. It also relates to the meso-structure thin film in which the orientation of a pore structure is controlled in a desired direction and manufacturing method therefor.

[0002]

[Description of the Prior Art] The porous materials are used in various fields, such as adsorption and separation. According to IUPAC, the porous materials are classified into as follows: microporous materials having a pore diameter of 2 nm or less; mesoporous materials having a pore diameter of 2 to 50 nm; and macroporous materials having a pore diameter of 50 nm or more. Known examples of the microporous material include zeolites such as natural aluminosilicates and synthetic aluminosilicates, and metal phosphates. These porous materials are employed for selective adsorption, shape-selective catalytic reactions, and

molecular-sized reactors by utilizing the pore size.

[0003] Known microporous crystalline materials have pore diameters of not more than about 1.5 nm. The synthesis of a solid having a larger pore diameter is demanded for adsorption and reaction of bulkier compounds not adsorbable by the micropore. As the materials having the larger pores, silica gels, pillared clays, and the like are known. However, these materials have a broad pore size distribution, and the pore size cannot be readily controlled.

[0004] With such a background, two methods have been disclosed at about the same time for synthesizing mesoporous silica having mesopores of a uniform size arranged in a honeycomb shape. The one method synthesizes a material called MCM-41 by hydrolysis of a silicon alkoxide in the presence of a surfactant, which is described in (Nature, vol. 359, p. 710). The other method synthesizes a material called FSM-16 by intercalation of an alkylammonium in interlaminar spaces of kanemite, a kind of layered polysilicate, which is described in (Journal of Chemical Society, Chemical Communications, vol. 1993, p. 680).

[0005] In both methods, it is considered that surfactant assembly serves as a template to control the structure of silica. These substances are useful as a catalyst for bulky molecules which cannot enter the pores of zeolite, and are promising in application as a functional material, for example, optical materials and electronic materials.

[0006] In application of such a mesoporous material having a regular porous structure as a functional material other than

catalysts, the technique for uniformly holding the material on a substrate is important. Examples of the method for forming a uniform mesoporous thin film on the substrate include a spin coating method as described in Chemical Communications, vol. 1996, p. 1149, and a dip coating method as described in Nature, vol. 389, p. 364, and a deposition for forming a film on the surface of a solid material by deposition as described in Nature, vol. 379, p. 703.

[0007]

[Problems to be Solved by the Invention] However, these conventional methods for forming the meso-structure thin film have the problems as described below. Namely, in the case of the normal spin-coated film, the direction of the centrifugal force acting on the precursor solution on the substrate is not controlled. Therefore, the meso-structure of the whole film does not have a directional configuration and thus the pores cannot be oriented. On the other hand, in the case of the method for precipitating the meso-structured material on the substrate, the substrate dependency of the formed film is large. For the formation of an oriented film, the substrate is limited to those having order at an atomic level like a cleavage plane of mica or graphite.

[0008] Therefore, there has been a need for a technique to form an inorganic oxide meso-structure thin film having an orientation on an optional substrate. As techniques for solving the problem, a method for controlling the pore direction using infiltration flow of the precursor solution disposed on a

substrate as described in "Nature, vol. 390, p. 674" and a method for controlling the pore direction by holding the substrate in the flow of solution as described in "Langmuir", vol. 15, p. 4544 have been proposed. However, these techniques need complicated apparatuses and further the shape of the thin film is limited.

[0009] The present invention was achieved in view of the problems of the conventional technique. An objective of the present invention is to provide the meso-structure thin film having orientational pores on the substrate and a simple method for forming the meso-structure thin film having orientational pores on the optional substrate.

[0010]

[Means for Solving the Problem] That is, according to the present invention, there is provided a meso-structure thin film formed by applying a precursor solution containing a surfactant and an inorganic oxide precursor material on a substrate using a centrifugal force, where tube like pores in the thin film are oriented almost parallel to the direction of the centrifugal force applied to the substrate.

[0011] Tube like pores of the meso-structure thin film may be filled with the surfactant or the meso-structure thin film may have a hollow structure formed by removing the surfactant from the tube like fine pores.

[0012] According to the present invention, there is provided a method for forming the meso-structure thin film by applying a precursor solution containing a surfactant and an inorganic

oxide precursor material on the substrate by spin coating, including the steps of preparing the precursor solution containing the surfactant and the inorganic oxide precursor material, holding the substrate outside the rotation center of a spin coater, and placing the precursor solution on the substrate and applying the solution by spin coating to form the meso-structure thin film.

[0013] Further, according to the present invention, there is provided a method for forming the meso-structure thin film by applying a precursor solution containing a surfactant and an inorganic oxide precursor material on the substrate by spin coating, including the steps of preparing the precursor solution containing the surfactant and the inorganic oxide precursor material, holding the substrate outside the rotation center of a spin coater, placing the precursor solution on the substrate and applying the solution by spin coating to form the meso-structure thin film, and removing the surfactant from tube like fine pores in the formed meso-structure thin film to form a hollow structure.

[0014]

[Embodiments of the Invention] Hereinafter, the present invention will be specifically described. Fig. 1 is a schematic view illustrating an example of the meso-structure thin film of the present invention. Fig. 1(a) is a schematic plan view and Fig. 1(b) is an AA line cross-sectional view. The meso-structure thin film of the present invention is formed by applying the precursor solution containing the surfactant and

the inorganic oxide precursor material on the substrate using the centrifugal force. The long axis direction of tube like pores 3 in a thin film 2 is oriented almost parallel to a direction 4 of a centrifugal force applied to a substrate 1.

[0015] In the present invention, the method for forming the meso-structure thin film by applying a precursor solution containing a surfactant and an inorganic oxide precursor material on the substrate by spin coating includes the steps of preparing the precursor solution containing the surfactant and the inorganic oxide precursor material, holding the substrate outside the rotation center of a spin coater, and placing the precursor solution on the substrate and applying the solution by spin coating to form the meso-structure thin film.

[0016] Fig. 2 is an outline view illustrating an example of the holding of the substrate in the present invention. In the spin coater to be used in the present invention, a substrate 12 which forms the meso-structure thin film is placed outside a rotation center 13 of the spin coater as shown in Fig. 2. In the usual spin coating, the substrate is placed on the rotation center 13 and thus a centrifugal force is applied in all directions radiating from the center of the substrate by rotation. On the other hand, in the present invention, a unidirectional centrifugal force indicated by an arrow is applied to the substrate 12.

[0017] It is known that tube like pores in the meso-structure are oriented in the flow direction when the flow of the precursor

solution is generated in forming the meso-structure thin film. Based on the orientation, the method for forming an orientational meso-structure thin film is examined (see, "Nature", vol. 390, p. 674).

[0018] In the spin coating, since the precursor solution on the substrate is moved in a radial direction, tube like pores tend to be oriented radiating from the center. However, a centrifugal force F relates to an angular velocity ω and a distance r from the center.

[0019]

[Equation 1]

$$F \propto r\omega^2$$

[0020] Therefore, the centrifugal force becomes weaker as it is closer to the rotation center. Theoretically, the centrifugal force at the central portion of the substrate is 0 and thus the orientation at the central portion becomes random. Consequently, it is difficult to achieve a clear radial orientation of the overall substrate.

[0021] In the present invention, since the substrate is placed outside the rotation center of the spin coater, a unidirectional force acts on the precursor solution on the substrate. As a result, the flow of the solution is caused, which allows tube like pores to be oriented in the direction of the centrifugal force.

[0022] Fig. 3 is an outline view illustrating an example of the substrate holder to be used for the present invention. Fig. 4 is a BB line cross-sectional view of the substrate holder of

Fig. 3.

[0023] The method for fixing the substrate on a substrate holder 11 of Fig. 2 is not particularly limited. A general method involves the steps of making the shaft of the spin coater hollow, connecting with a vacuum pump, and vacuum chucking with the substrate holder 11 having the structure shown in Fig. 3. The state that the substrate 12 is fixed on the substrate holder 11 will be described with reference to the cross-sectional view of Fig. 4. In Fig. 4, a space between the substrate 12 and the grooves 22 provided on the substrate holder 11 is in a vacuum state by a vacuum pump through a hole 23 formed in the center of the groove and a cavity 24 which connects a shaft 21 of the spin coater and the substrate 12 is fixed on the substrate holder 11.

[0024] The precursor solution containing the surfactant and the inorganic oxide precursor material are dropped on the substrate fixed on the substrate holder. The precursor solution to be used in forming the meso-structure thin film of the present invention is a mixture prepared by mixing a solution prepared by adding a catalyst to a solvent containing at least a surfactant and an inorganic oxide precursor of a compound that form inorganic oxide by hydrolysis polycondensation. The precursor solution may be a known solution.

[0025] The surfactant is suitably selected from nonionic surfactants which contain quaternary alkylammonium and polyethylene oxide as a hydrophilic group. The length of surfactant molecules to be used is determined depending on the

pore diameter of a targeted meso-structure. In order to increase the diameter of surfactant micelle, an additive, for example, mesitylene may be added.

[0026] Examples of the catalyst include an acid such as hydrochloric acid and a base such as sodium hydroxide. Particularly, hydrochloric acid is preferable. Further, the usable solvent is not particularly limited as long as the surfactants, catalysts, and the compound which forms inorganic oxide can be dissolved therein. Particularly, water and alcohol are preferable.

[0027] Examples of the oxide precursor material which forms inorganic oxides include halide and alkoxide. The oxide to be formed is not particularly limited. Preferable examples thereof include silicon oxide, titanium oxide, tin oxide, zirconium oxide, gallium oxide, aluminium oxide, and vanadium oxide. It may be a composite oxide of two or more elements.

[0028] The material of the substrate to which the precursor solution is applied is not particularly limited and a wide range of materials can be used. Usable examples thereof include glass, ceramics, and resins. However, it is necessary to select the materials which do not react with the precursor solution.

[0029] The surface of the substrate may be subjected to orientation treatment. The orientation treatment is the same as that used for orientation of liquid crystals. Known methods, such as rubbing treatment and oblique evaporation can be used. In this case, it is necessary to match the orientation direction by orientation treatment to the direction of the centrifugal

force at the time of spin coating.

[0030] When the substrate is fixed on the substrate holder and then the spin coater is rotated after dropping the precursor solution, the solution on the substrate is circumferentially moved by the centrifugal force. The use of the flow allows for directional control of micelles in the present invention, namely, orientation control of the pore structure. The number of rotations is determined according to the thickness. The uniaxial orientation of pores is higher as the number of rotations is higher, which results in the formation of a film having a thin layer.

[0031] It is preferable that the centrifugal force largely acts on the substrate holder, and thus it is advantageous to have a large radius. The fixed position of the substrate is preferably as close to the outside of the substrate holder as possible. It is desirable to design an optimal substrate holder in the acceptable range based on the size of the spin coater to be used. The orientation of pores of the meso-structure is influenced by the centrifugal force, solution viscosity, surfactant species to be used, oxide precursor species, solvent species, substrate, temperature, and humidity. Therefore, even when the substrate is held so as to maintain the same distance from the rotation center, the same orientation cannot always be obtained.

[0032] The material of the substrate holder is not particularly limited as long as it is resistant to chemicals (e.g. acid). Usable examples thereof include stainless steel, polypropylene,

and Teflon (registered trademark). The substrate holder that can fix four substrates is shown in Fig. 3. The substrate holder may have a structure that can hold more substrates in the position symmetrical to the center along a circle and the same position.

[0033] It is preferable that the whole spin coater is placed in a space where the temperature and humidity are adjusted. The temperature and humidity are optimally controlled according to the target oxide, the type of the surfactant and the solvent. The film thus formed on the substrate is dried and an oxide meso-structure thin film in which the surfactant is held in pores is obtained.

[0034] A meso-structure thin film having a hollow structure can be formed by removing surfactant micelle of the template from the meso-structured material. The removal of the surfactant is selected from firing, solvent extraction, supercritical fluid extraction, degradation by ultraviolet radiation and the ozone generated at the time, and degradation by an ozone aqueous solution. For example, the surfactant can be removed completely by firing the meso-structure thin film at 550°C in the air for 10 hours almost without destroying the meso-structure. Although it is difficult to remove 100% of surfactant by solvent extraction process, a mesoporous thin film can be formed on a substrate of a material vulnerable to firing.

[0035]

[Examples] Hereinafter, the present invention will be further specifically described with reference to examples.

[0036] Example 1

The used substrate was a 38 mm (1.5 inches) square alkali-free glass (manufactured by Corning INC, 7059) which had been washed with acetone, isopropyl alcohol, and pure water and subjected to surface cleaning in an ozone generator.

[0037] Polyethylene oxide 10 cetyl ether of 6.0 g (manufactured by Aldrich) was dissolved in 62 ml of water. Tetramethyl orthosilicate of 8.2 ml (manufactured by Kishida Chemical Co., Ltd.) was added thereto, which was heated to 80°C and stirred so as to be a homogeneous solution. Concentrated hydrochloric acid of 0.5 ml (about 35%, manufactured by Kishida Chemical Co., Ltd.) was added to the homogeneous solution, which was stirred at 80°C at 500 mmHg for 30 minutes and the resulting solution was used as the precursor solution.

[0038] A meso-structure thin film was formed using a spin coater mounted on a constant temperature and humidity bath at 25°C and 60% R.H.. The used substrate holder in which four substrates could be held by vacuum chucking was the same as that shown in Fig. 3. The coat solution was dropped on the glass substrate which was placed close to a circular substrate holder with radius 17 cm at the position where there was a 160 mm distance between the end portion of the substrate and the center of rotation, followed by rotating the coater at 2000 rpm for 30 seconds. Thereafter, the glass substrate was dried in the air at room temperature for 12 hours and a transparent silica meso-structure thin film was formed.

[0039] The substrate on which the silica meso-structure thin film was formed was analyzed by X-ray diffraction. As a result,

a major diffraction peak assigned to the (100) plane of a hexagonal structure having an interplanar spacing of 4.37 nm was observed. It was confirmed that the thin film had a hexagonal pore structure. The absence of diffraction peak in the wide-angle region shows that the silica constituting the wall is amorphous.

[0040] The uniaxial orientation of the mesochannel of the meso-structured silica thin film was evaluated quantitatively by in-plane X-ray diffraction analysis. The method described in ("Chemistry of Materials", vol. 11, p. 1609) measures the dependency of the X diffraction strength assigned to the (100) plane perpendicular to the substrate on the in-plane rotation. The orientation direction and distribution of mesochannels can be checked by the method. The silica meso-structure thin film formed in Example 1 was measured. The dependency of the (110) plane diffraction intensity on the in-plane rotation angle is shown in Fig. 5. In the measurement, the direction of centrifugal force acting on the substrate was 0°. As shown in Fig. 5, a Gaussian type profile centered at 0° was obtained. This shows that, in the silica meso-structure thin film prepared in Example 1, the mesochannels are oriented in the direction parallel to the centrifugal force at the time of spin coating with the half width of the distribution of the orientation direction being about 46°.

[0041] The substrate having the silica meso-structure thin film was placed in a muffle furnace, heated at a heating rate of 1°C/min up to 550°C, and fired in the air for 10 hours. Great differences

between the surface of the fired substrate and the surface of the pre-fired substrate were not seen. The X-ray diffraction analysis of the fired thin film gave an intense diffraction peak assigned to the (100) plane of a hexagonal structure having an interplanar spacing of 3.44 nm, resulting in showing the retention of the hexagonal pore structure. After the firing, no diffraction peak was observed in the wide-angle region, which shows that the silica of the wall was kept amorphous. The sample after the firing was confirmed not to contain organic components resulting from the surfactant by infrared absorption spectrum.

[0042] In order to examine the orientation of pores as to the sample after firing, the in-plane X-ray diffraction analysis was carried out. In this case, the dependency of the (110) plane diffraction intensity on the in-plane rotation angle was measured. As the result, a profile almost similar to that of the meso-structure thin film before the firing was given. It was confirmed that the orientation of the pore was completely maintained.

[0043] The thin film before the firing and the thin film after the firing were cut perpendicularly to the direction of the centrifugal force and the sectional faces were observed with a transmission electron microscope. Pores having a hexagonal structure were found in the sectional faces of both thin films and tube like channels were oriented in the direction of the centrifugal force.

[0044] Comparative example 1

A silica meso-structure thin film was formed in the same

manner as in Example 1 except that a usual spin coating method in which the substrate is adhered to the spin coater so as to match the center of gravity of the substrate to the shaft of the spin coater was used.

[0045] When the substrate having the silica meso-structure thin film was analyzed by X-ray diffraction analysis, an intense diffraction peak assigned to the (100) plane of a hexagonal structure having an interplanar spacing of 4.43 nm was observed. This showed that the thin film had the hexagonal pore structure. The absence of diffraction peak in the wide-angle region shows that the silica constituting the wall is amorphous.

[0046] In order to examine the orientation direction of tube like pores as for the thin film sample, the in-plane X-ray diffraction analysis was carried out. The dependency of the diffraction intensity assigned to the (110) plane perpendicular to the film surface on the in-plane rotation angle was measured in the same manner described in Example 1. In this case, the position of 0° can be set to any direction. The observed profile is substantially flat to the angle of rotation, which shows that there is little in-plane structural anisotropy.

[0047] Comparative example 1 showed that a meso-structure having an orientation of tube like pores could not be formed when spin coating was performed matching the center of the substrate to the shaft.

[0048] Example 2

Example 2 shows an example of the formation of a tin oxide meso-structure thin film having tube like pores which are

unidirectionally oriented by the spin coating method of the present invention. Polyethylene oxide 10 stearyl ether of 2 g (manufactured by Aldrich) was dissolved in 20 g of ethanol (manufactured by Kishida Chemical Co., Ltd.). After dissolving completely, tin chloride of 5.2 g ($SnCl_4$) was added thereto. The mixed solution was stirred for 30 minutes and then 1 g of pure water was added thereto, which was used as the precursor solution.

[0049] The spin coater mounted on the constant temperature and humidity bath at 25°C and 60% R.H., the substrate holder, and the glass substrate which were the same as Example 1 were used and the coater was rotated at 2000 rpm for 30 seconds to form a film. The resulting film was left and dried at room temperature for 72 hours and a tin oxide meso-structure thin film was formed.

[0050] When the thin film was analyzed by the X-ray diffraction analysis, an intense diffraction peak assigned to the (100) plane of a hexagonal structure having an interplanar spacing of 4.75 nm was observed. This showed that the thin film had the hexagonal pore structure.

[0051] When the thin film was analyzed by the in-plane X-ray diffraction analysis, the diffraction peak assigned to the (100) plane perpendicular to the film surface was observed. The dependency of the diffraction intensity of the peak on the in-plane angle was measured. In this case, the direction of centrifugal force acting on the substrate was 0°. As the result, the Gaussian type profile centered at 0°was observed in the tin oxide meso-structure thin film formed in Example 2 as with

Example 1. It was revealed that tube like pores were oriented in the direction of the centrifugal force. From the half width, it is found that the half width of the distribution of mesochannels is about 52°.

[0052] As apparent from Examples, it is found that the tin oxide meso-structure thin film having uniaxially oriented tube like fine pores can be formed by the method of the present invention.

[0053]

[Effect of the Invention] As described above, according to the present invention, the meso-structure thin film having orientational tube like fine pores on an optional substrate and the mesoporous thin film can be formed by holding the substrate outside of the shaft of the spin coater in spin coating and applying a unidirectional centrifugal force to the precursor solution on the substrate.

[Brief Description of the Drawings]

[Fig. 1] Fig. 1 is a schematic view illustrating an example of the meso-structure thin film of the present invention.

[Fig. 2] Fig. 2 is an outline view illustrating an example of the holding of the substrate in the present invention.

[Fig. 3] Fig. 3 is an outline view illustrating an example of the substrate holder to be used for the present invention.

[Fig. 4] Fig. 4 is a BB line cross-sectional view of the substrate holder of Fig. 3.

[Fig. 5] Fig. 5 is a view illustrating the profile which shows the dependency of the (110) plane diffraction intensity on the in-plane rotation angle of the sample in the in-plane X-ray

diffraction analysis when observing the silica meso-structured material formed in Example 1 of the present invention.

[Description of the Symbols]

1 Substrate

2 Thin Film

3 Fine pore

4 Direction of centrifugal force

11 Substrate holder

12 Substrate

13 Center of rotation

21 Hollow shaft

22 Groove

23 Hole formed in the center of the groove

24 Cavity

Fig. 1

1 Substrate

2 Thin Film

3 Fine pore

4 Direction of centrifugal force

Fig. 2

11 Substrate holder

12 Substrate

13 Center of rotation

Fig. 3

11 Substrate holder

12 Substrate

21 Hollow shaft

22 Groove

23 Hole formed in the center of the groove

24 Cavity

Fig. 4

11 Substrate holder

12 Substrate

21 Hollow shaft

22 Groove

23 Hole formed in the center of the groove

24 Cavity

Fig. 5

Plane diffraction intensity (cps)

In-plane rotation angle (°)